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The fluorescence of 7-aminocoumarins is quenched by a variety of organic electron donors or acceptors in acetonitrile. In general, donors with half-wave oxidation potentials less positive than 1.0V vs SCE and acceptors with reduction potentials less negative than -1.5V vs SCE are candidates for diffusion limited quenching of coumarin fluorescence. In flash photolysis experiments electron transfer for several dyes and quenchers is demonstrated. Electrochemical properties of dyes have been investigated by cyclic voltammetry.

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ELECTRON DONOR-ACCEPTOR QUENCHING AND PHOTOINDUCED

ELECTRON TRANSFER FOR COUMARIN DYES

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Abstract

The fluorescence of 7-aminocoumarins is quenched by a variety of organic
electron donors or acceptors in acetonitrile. In general, donors with
half-wave oxidation potentials less positive than 1.0 V vs SCE and
acceptors with reduction potentials less negative than -1.5 V vs SCE are
candidates for diffusion limited quenching of coumarin singlet states.
Profiles of quenching rates are consistent with calculated free energies
for electron transfer between excited coumarins and donors or acceptors.
In flash photolysis experiments electron transfer for several dyes and
quenchers (e.g., methyl viologen) is demonstrated. Relatively low yields
of net electron transfer are consistently obtained due to inefficient ionic
photodissociation via singlet quenching or a low yield of more photoactive
coumarin triplets. Electrochemical properties of the coumarins have been
investigated by cyclic voltammetry with the indications of reversible
oxidation and irreversible reduction as important processes.

The 7-aminocoumarins (e.g., 1 - 5) constitute an important class of organic dyes which lase [2] and which in some circumstances may act as photosensitizers.[3,4] These structures are also related to the furocoumarins which have received much attention due to their photobiological properties.[5] In previous papers in this series, photophysical and photochemical properties for coumarin dyes have been reported with particular attention given to the pronounced medium dependences of spectral properties and emission yields associated with the highly polar coumarin excited states (nominally depicted by 6).[6] Other recent investigations have been directed to the mechanism of coumarin photodegradation, [7] the behavior of coumarin dyes in water and in aqueous detergent media, [8] and the effects of medium and additives on photostability and emission yield under lasing conditions.[9 - 11]

The coumarin dyes give rise to strong, broad absorption bands extending into the visible accompanied by solvent dependent red shifts in emission indicative of an emissive state having a large dipole moment (i.e., 6). The interaction of such excited species with added quenchers has not been studied in detail although coumarin singlet [10, 12] and triplet [13] quenching by oxygen have been reported. Our expectation was that the internal combination of donor and acceptor groups for the aminocoumarins would activate the intramolecular charge transfer state toward quenching by both reducing and oxidizing agents. This feature would in turn dictate to a significant degree the bimolecular photochemistry displayed by coumarin dyes and also prescribe the types of reagents that might be suitable as

additives to dye solutions (agents that might insure photostability). We
report here the behavior of representative aminocoumarins toward electron
transfer agents in acetonitrile , the detection of products resulting from
photoinduced electron transfer, and related electrochemistry for the dyes.

Experimental Section

Materials. Dyes $\underline{1}$ - $\underline{5}$ were laser grade materials obtained from
Eastman Kodak Co. (coumarins 1, 35, 102, 153, and 6, respectively). The
dyes were checked for purity by tlc (silica, ethyl acetate/hexane) and in
most cases used as received. Several of the commercial samples were
recrystallized from heptane or methanol/water. The amine quenchers and DMM
were distilled prior to use; DMA was dried by addition of lithium aluminum
hydride under nitrogen prior to distillation under reduced pressure (20
torr). FUM was recrystallized three times from hexane/chloroform and DCB
and MV were recrystallized twice from methanol. Solvents employed were
spectroquality acetonitrile used as received and triply distilled water.

Fluorescence quenching. Dye emission was recorded on a Perkin-Elmer
MPF 44A fluorimeter equipped with a spectrum correction unit and using
quartz cells. Solutions of 10^{-5} M dye were excited at the absorption
maximum and the fluorescence intensity (at λ_{max}) recorded as a function of
added quencher (samples were air saturated). Except for the cases noted
below, no changes were recorded in the emission maximum or in the dye
absorption profile as the result of addition of quencher. Intensity
changes were plotted vs. quencher concentration using the Stern-Volmer

equation, $Io/I = 1 + k_q\tau$ [Q]. Linear regression analysis ($r = > 0.98$) provided slopes ($k_q\tau$ values) and intercepts (typically $1.00 + 0.02$).

Triplet quenching. Flash photolysis. Flash photolysis apparatus which consisted of a Xenon flash lamp with ca. 35μs duration (fwhm) (22 cm Pyrex cell) has been described previously.[14] Argon-purged solutions of ca. 10^{-5}M dye were employed. Photographs of oscilloscope traces were obtained to record % transmission values which were converted to transient absorbance. For measurement of relative yield of transients, absorbance values were recorded at their maximum at the shortest practical times following lamp discharge (usually 100μs following the flash).

Cyclic voltammetry. Current-voltage curves were obtained for 10 mM dye in reagent grade (wet) acetonitrile with 0.1 M tetraethylammonium perchlorate (TEAP) or 0.1 M $LiClO_4$ supporting electrolyte using a Bioanalytical Systems potentiostat. Other conditions included: working electrode, Au or Pt; reference electrode , Ag, $AgNO_3$ (0.01 M); auxiliary electrode, Pt; operating temperature 22°.

Results and Discussion

Coumarin dye properties: cyclic voltammetry. Absorption and fluorescence emission data for dyes $\underline{1} - \underline{5}$ are shown in Table 1 along with fluorescence lifetimes appropriate for air-saturated acetonitrile solutions at room temperature. In Table 2 are included values for oxidation and reduction potentials for the dyes obtained by cyclic voltammetry for

acetonitrile solutions. The electrochemical oxidations were characterized by relatively clean forward and return waves with 60 - 100 mV peak to peak separation consistent with quasi-reversible behavior.[16] The dyes were somewhat more difficultly reduced (a peak potential could not be measured for 3) and reduction return waves were not observed. Due to the irreversibility of reduction of the dyes in acetonitrile, peak potentials which varied somewhat according to scan rate (100 - 500 mV/s) represent rough approximations to the thermodynamic reduction potentials.

The substituent influences for dye reduction and oxidation are readily apparent in terms of the lactone moiety and other groups such as CF_3 providing a retarding influence on oxidation (relative to dialkylanilines for which E_{ox} = ca. 0.7 V vs SCE^{17}). Alkyl substitution at the aniline ring provides for greater ease of oxidation whereas the series is less readily reduced due to these electron donating influences (relative to unsubstituted coumarin for which E_{red} = -1.4 V vs SCE^{16}).

<u>Singlet quenching by electron donors and acceptors</u>. The selection of potential quenchers of dye fluorescence is shown in Table 3 along with the appropriate electrochemical data which reflect their relative strengths as oxidizing or reducing agents in acetonitrile. The results of Stern-Volmer analysis of steady-state emission quenching by the electron donor amines are assembled in Table 4. DMA is sufficiently potent to quench the fluorescent state of three of the dyes (1, 2, and 4) at rates which approach the diffusion controlled limit (ca. 2-3 x 10^{10} $M^{-1}s^{-1}$).[18] The exception involves the least readily reduced dye, 3, for which a diminished rate is observed. Consistent with this indication of dominant

donor-acceptor influence is the trend established for quenching 2 fluorescence in which rate constants fall in a regular fashion according to amine oxidation potential. If a near-diffusion- limited value for kq is supplied for DMA quenching of 5 a quite reasonable value for the lifetime of emission for this dye (not presently available from photon counting measurements) is obtained (Table 1).

A similar series of quenching data involving various electron acceptors is reproduced in Table 5. Again, one common quencher, FUM, is successful in sequestering coumarin singlets at a high rate. The more potent acceptor, MV, 1,1'-dimethyl-4,4'-bipyridinium dication, requiring for solubility considerations a mixed aqueous medium , is somewhat more successful in quenching 1 fluorescence (reaching the diffusion limited rate). When less effective oxidizing quenchers are inspected for 5, fall-off of the quenching constants is again observed, consistent with a diminished quencher reduction potential.

Quenching data may be analyzed using the Weller equation.[19]

$$\Delta G_{et} = E_{ox} - E_{red} - E_{00} - C$$

with which the free energy change for an encounter pair undergoing electron transfer is computed using redox potentials (converted to energies), the excitation energy of the excited state participating in quenching (E_{00}, for coumarin singlets, computed from absorption and emission curves), and a

coulombic term, C, usually assumed to value ca. 0.1 eV for acetonitrile solvent.

Computed free energies are provided in Tables 4 and 5. The "rule of thumb"[19] which suggests that near diffusion limited quenching behavior is observed in bimolecular quenching via electron transfer when $\Delta G_{et} \leq -5.0$ kcal/mol is again valid for the coumarin quenching data. The pattern of free energy dependence shown by the data for $\underline{2}$ and $\underline{5}$ reflects a diminution in quenching constant of about one order of magnitude for each reduction in electron transfer exothermicity of 5 - 10 kcal/mol. A similar dependence for organic donors and acceptors in excited state quenching has been found in a variety of other systems.[30,31]

Triplet quenching. Flash photolysis. The coumarins in combination with several quenchers were subjected to flash irradiation using conventional equipment (Xenon flash lamp, 35µs fwhm). Under conditions where quencher concentrations dictated that coumarin singlets were substantially quenched (from Stern-Volmer analyses, vide supra), transients were not generally observed in the 450 - 700 nm range (100 µs to 100 ms regime). Such combinations included $\underline{1}$ and $\underline{2}$ with DMA and FUM. Spectra for coumarin radical-ions have not yet been reported, but transients such as DMA$^+$ ($\lambda_{max} \cong 500_{nm}$)[22] are readily observed. The failure of singlet quenching in providing even moderate yields of radical- ions in bulk solution is consistent with a number of recent findings which show that the fate of singlet radical-ion pairs resulting from exothermic electron transfer quenching is predominantly in-cage recombination.[23,24]

The search for electron transfer products from quenching was combined with the detection of triplet-triplet absorption for two of the dyes. For 1 alone in acetonitrile or in 85% acetonitrile/water, a transient with λ_{max} at 600 - 625 mm was observed and assigned to the coumarin triplet which has been detected previously.[7,13,14] The triplet of 1, which showed a first order decay and a lifetime of 120-180 μs (several runs) in acetonitrile could be completely quenched by 1.0 mM FUM (where singlet quenching is not important). In this experiment the 600 mm transient is not replaced by another absorbing species in the 400 - 700 region (the FUM radical-anion absorbs at 350 mm,[26] an area obscured by dye bleaching and recovery). DMA (1.0 mM), on the other hand, is not successful in intercepting triplet 1. Both of these results are consistent with electron (or energy) transfer quenching by FUM but not by DMA if the energetics of Tables 4 and 5 are modified by reducing the exothermicity of electron transfer by ca. 10 kcal/mol, the estimated difference in singlet and triplet energies for similar dyes as shown by recent spectroscopic measurements. [3,27]

Exceptions to the general pattern of negligible reactivity (net electron transfer) were encountered for the acceptor quencher, MV.[28] Flash photolysis of 1 and 5 was examined in some detail under conditions appropriate for quenching by MV of dye singlets or triplets. A transient similar to triplet 1 was observed on flash irradiation in the presence of MV (Table 6). The absorption maximum was again at about 600 mm, consistent with formation of the reduced species MV^+.[28] (The other well characterized absorption of MV+ at 395 mm is obscured by strong absorption by the dye in that region.) That this transient observed with added MV is clearly a species other than the dye triplet is indicated by the extended decay time

(millisecond range) which is more consistent with the appearance of a radical-ion. Decay data for the presumed MV^+ intermediate did not uniformly obey first or second order kinetics and decay times (reported as half-lives, Table 6) varied somewhat from run to run and were sensitive to sample preparation (Ar purging).

The dependence of yield of electron transfer was inspected for 1 as a function of MV concentration in acetonitrile/water. A moderate increase in maximum absorbances (Table 6) recorded at about 100μs following the lamp flash (prior to the onset of significant decay) is noted for increased concentrations of MV. Absolute values for electron transfer yield were not determined but were clearly quite low, as suggested by data for viologen quenching in other well characterized systems.[28,29] The relative yields reported here are consistent with an inefficient photoinduced electron transfer for coumarin singlet quenching (vide supra) and a more robust reaction of the coumarin triplet whose yield in the absence of quencher (via intersystem crossing) is known to be very low (< 1% for 1 in acetonitrile;[8] (Concentrations of MV = 4.0 and 10.0 mM correspond to 20% and 40% singlet quenching , respectively.)

Electron transfer involving 5 and methyl viologen appears also to be important (Table 6). Yields of electron transfer for 1 and 5 appear similar but the comparison is complicated since triplet yields (or triplet extinction coefficients) for both dyes are not known.[30,31]

In summary, the quenching of the fluorescence of coumarin laser dyes by a variety of electron donors and acceptors has been observed. Net electron transfer is not a dominant path for donor-acceptor quenching,
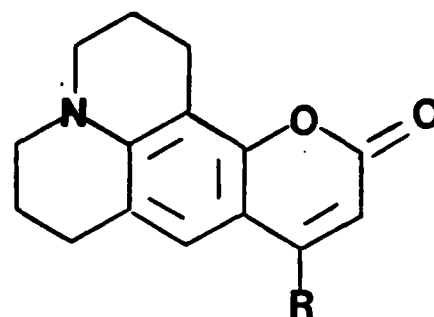
although the photoreduction of methyl viologen on quenching of dye singlets or triplets is confirmed by flash photolysis results. The ranges of oxidation and reduction potential for additives which will diminish the fluorescence of several representative coumarin dyes have been established.

$(CH_3CH_2)_2N$
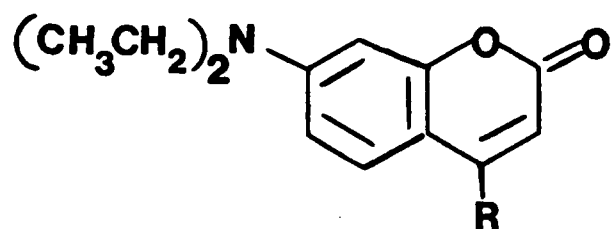
1, R = CH$_3$

2, R = CF$_3$

3, R = CH$_3$

4, R = CF$_3$

$(CH_3CH_2)_2N$
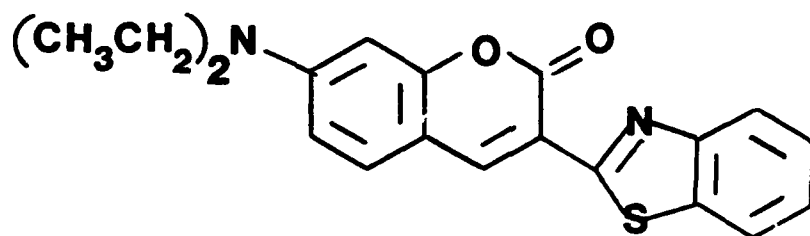
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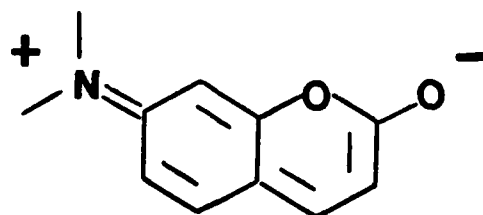
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28. For a review of data concerning electron transfer to MV, see Kalyanasundaram, _Coord. Chem. Rev._, 1982, 159.

29. In a crude comparison (where absorbanced cannot be exactly matched) the well characterized system, ruthenium(II)-trisbipyridyl and MV in H_2O, ϕ_{et} = 0.2–0.3,[28] produces on flash photolysis the viologen radical in a yeild at least ten-fold greater than the system, 1/MV in acetonitrile/water.

30. Dempster, et al.,[25] report ε = 19,000±2,000$M^{-1}cm^{-1}$ for triplet 1 in ethanol, also to be compared with a value of 14,000$M^{-1}cm^{-1}$ for MV in water.
   A weak transient ($\lambda_{max} \sim 500nm$) can be observed on quenching 1 with DMA in acetonitrile. This absorption is much like that of the DMA radical-cation.[22]

Table 1   Absorption and emission properties of coumarin dyes in acetonitrile

	λ_a	λ_f	$\tau_f{}^b$, ns
1	367	434	2.8
2	396	501	0.60
3	380	451	2.8
4	418	521	4.6
5	454	501	$(3.1)^c$

[a]Absorption (λ_a) and emission (λ_f) maxima in nm.

[b]Fluorescence lifetimes reported for N_2 or Ar purged solutions (ref. 6) corrected for fluorescence quenching by O_2 in air saturated solutions (ref. 6c)

[c]Obtained from dimethylaniline quenching results (see text).

Table 2   Redox potentials for coumarin dyes from cyclic voltammetry

	E_{ox} (V vs SCE)[a]	E_{red} (V vs SCE)[b]
1	1.09	-2.2
2	1.20	-1.8
3	0.72	<-2.3
4	0.89	-1.8
5	1.02	-1.5

[a]Oxidation potentials from reversible waves calculated as $[E_p(ox) + E_p(red)]/2$ (CH$_3$CN)

[b]Reduction (peak) potentials from irreversible waves (CH$_3$CN)

Table 3. Electron donor or acceptor quenchers[a]

Electron donor	E_{ox}(V vs SCE)	Electron acceptor	E_{red}(V vs SCE)
diethylamine (DEA)	2.2	dimethyl maleate (DMM)	-1.6
triethylamine (TEA)	1.1	p-dicyanobenzene (DCB)	-1.7
dimethylaniline (DMA)	0.73	fumaronitrile (FUM)	-1.3
		methyl viologen (MV)	-0.69

[a]Redox potentials = half-wave potentials from polarography or cyclic voltammetry of quenchers in acetonitrile (ref 17).

Table 4. Fluorescence quenching data for coumarins and electron donors

Dye	Quencher	$k_q\tau, M^{-1}$	$k_q (\times 10^{-9} M^{-1}s^{-1})$	ΔG_{et}[a]
1	DMA	27.	9.7	-4.6
2	DEA	<0.10	<0.17	28.
	TEA	1.5	2.5	4.0
	DMA	11.	18.	-5.7
3	DMA	6.7	2.4	>-1.2
4	DMA	50.	11.	-4.6
5	DMA	31.	(10.)	-8.3

[a]Free energy change for electron transfer (kcal/mol) calculated using the Weller equation (see text).

Table 5. Fluorescence quenching data for coumarins and electron acceptors

Dye	Quencher	$k_q\tau, M^{-1}$	$k_q(\times 10^{-9} M^{-1}s^{-1})$	ΔG_{et}^a
1	FUM	29.	8.7	-17
	MV[b]	81.	29.	-31
2	FUM	3.5	5.8	-6.8
3	FUM	66.	24.	-23.
4	FUM	25.	5.4	-11.
5	DCB	<0.2	<0.06	2.2
	DMM	0.6	0.2	0.8
	FUM	31.	9.7	-6.8

[a]Free energy change for electron transfer (kcal/mol) calculated using the Weller equation (see text).

[b]Quenching results for 85% CH_3CN/H_2O, assuming $\tau_f(1) = 2.8$ ns, the value for CH_3CN (Table 1).

Table 6. Transient absorption on flash photolysis of 1 and 5 with MV[a]

	[MV], mM	A_{600}	$\tau_{1/2}$, ms	Assignment
1	-	0.28	0.16	triplet 1
	0.02	0.25	1.3	MV radical-ion
	4.0	0.57	4.8	MV radical-ion
	10.0	0.67	1.3	MV radical-ion
5	-	0.02	0.3	triplet 5
	0.04	0.65	1.4	MV radical-ion

[a]Absorbances recorded at 600 nm, 100 us after flash (argon-purged 85% v/v CH_3CN/H_2O).

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